

TRIPHENYLPHOSPHINE COMPLEXES OF Cu(I), Ag(I) AND  
Au(I) N,N-DIALKYLDITHIOCARBAMATES.

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(Received 7 August 1970)

The synthesis and properties of bis-triphenylphosphine complexes of Cu(I) and Ag(I) N,N-dialkyldithiocarbamates  $[(\text{Ph}_3\text{P})_2\text{M}(\text{R}_2\text{dtc})]$  were reported by Kowala and Swan (1). Molecular weights of these compounds in benzene or chloroform were 30 - 50% lower than the calculated values. In spite of the low conductivities in chloroform and nitrobenzene solutions Kowala and Swan suggested that these complexes are best formulated as  $(\text{Ph}_3\text{P})_2\text{M}^+\text{R}_2\text{dtc}^-$ . We have reinvestigated the  $\text{Et}_2\text{dtc}$  complexes, and have also succeeded in preparing  $(\text{Ph}_3\text{P})_2\text{Au}(\text{Et}_2\text{dtc})$ . Conductivity studies in nitrobenzene show the Cu, Ag and Au complexes to be non-electrolytes (at a concentration of  $10^{-2}$  mole/l the molar conductivity is lower than  $0.1 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ ). Osmometrically determined molecular weights are summarized in the TABLE. The combined results clearly indicate a dissociation:



It is noteworthy that the dissociation increases in the order  $\text{Cu} < \text{Ag} < \text{Au}$ . Our finding that the Au complex in benzene is completely dissociated, is confirmed by the synthesis of  $(\text{Ph}_3\text{P})\text{Au}(\text{Et}_2\text{dtc})$  which is monomeric in benzene solution (TABLE).

Attempts to prepare  $(\text{Ph}_3\text{P})\text{M}(\text{Et}_2\text{dtc}) \dots \text{M} = \text{Cu}, \text{Ag}$  were unsuccessful. In contrast with the report by Kowala and Swan addition of methyl iodide to a solution of the bis-phosphine complexes in benzene results in the formation

TABLE

Molecular weights of  $(\text{Ph}_3\text{P})_2\text{M}(\text{Et}_2\text{dtc})$  and  $(\text{Ph}_3\text{P})\text{Au}(\text{Et}_2\text{dtc})$  in benzene at  $37^\circ$ .

	Found	Calc.
$(\text{Ph}_3\text{P})_2\text{Cu}(\text{Et}_2\text{dtc})$	600	736
$(\text{Ph}_3\text{P})_2\text{Ag}(\text{Et}_2\text{dtc})$	450	781
$(\text{Ph}_3\text{P})_2\text{Au}(\text{Et}_2\text{dtc})$	430	870
$(\text{Ph}_3\text{P})\text{Au}(\text{Et}_2\text{dtc})$	600	607

of methyltriphenylphosphonium iodide, supporting the idea of dissociation into free phosphine.

#### EXPERIMENTAL

Molecular weight determinations were performed using the Hewlett Packard vapour pressure osmometer 302 B.

$(\text{Ph}_3\text{P})_2\text{M}(\text{Et}_2\text{dtc})$  ... M = Cu, Ag were prepared as previously reported (1).

$(\text{Ph}_3\text{P})_2\text{Au}(\text{Et}_2\text{dtc})$  was prepared on addition of two moles  $\text{Ph}_3\text{P}$  to 1 mole  $\text{Au}(\text{Et}_2\text{dtc})$  (2) in acetone solution. Colourless needles were obtained, m.p.  $134-136^\circ$ .

Anal. Found: C, 56.4; H, 4.4; Au, 22.7. Calc. for  $(\text{Ph}_3\text{P})_2\text{Au}(\text{Et}_2\text{dtc})$ : C, 56.6; H, 4.6; Au, 22.6%.

$(\text{Ph}_3\text{P})\text{Au}(\text{Et}_2\text{dtc})$  was prepared by adding equivalent amounts of  $\text{Na}(\text{Et}_2\text{dtc}) \cdot 3\text{H}_2\text{O}$  (Fluka A.G.) in ethanol to a solution of  $(\text{Ph}_3\text{P})\text{AuCl}$  (3) in  $\text{CH}_2\text{Cl}_2$ . NaCl was filtered off and, the solvent was evaporated under vacuo.

The residue was recrystallized from ethanol. Light yellow needles were obtained, m.p.  $152-153^\circ$ .

Anal. Found: C, 46.0; H, 4.1; N, 2.3; S, 10.5; Au, 32.4. Calc. for  $(\text{Ph}_3\text{P})\text{Au}(\text{Et}_2\text{dtc})$ : C, 45.5; H, 4.1; N, 2.3; S, 10.6; Au, 32.5%.

#### ACKNOWLEDGEMENT

The investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation for

the Advancement of Pure Research.

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